REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE June 29, 2001	3. REPORT TYPE AND DATES COVERED Final Report March 1998-~~March 2001~~ 01 25 Feb 01

4. TITLE AND SUBTITLE
Designing Polymer Blends Through Modeling and Simulation

5. FUNDING NUMBERS
DAAG559810115

DAAG55-98-1-0115

6. AUTHOR(S)
Anna C. Balazs, David Jasnow

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Pittsburgh

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

37574.7-CH

11. SUPPLEMENTARY NOTES

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Using theoretical models and computer simulations, we determined guidelines for promoting the uniform dispersion (exfoliation) of clay sheets in polymer melts. In addition, we determined how the coupling between phase separation and wetting interactions in polymeric composites effects the structural evolution and phase behavior of the material. We also developed a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, and theory predicts new ordered phase, where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

14. SUBJECT TERMS
Polymer blend, composites, modeling, simulation, theory

15. NUMBER OF PAGES
3

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
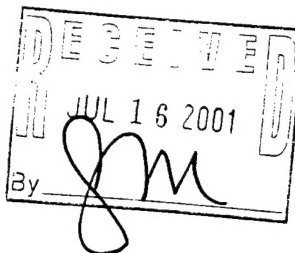Prescribed by ANSI Std. 239-18
298-102

Enclosure 1

RECEIVED
JUL 16 2001
By

20010801 016
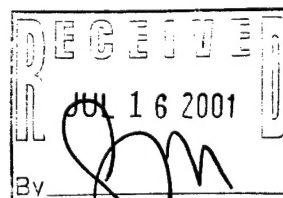
MEMORANDUM OF TRANSMITTAL

U.S. Army Research Office
ATTN: AMSRL-RO-BI (TR)
P.O. Box 12211
Research Triangle Park, NC 27709-2211

RECEIVED
JUL 1 6 2001
By _____

☐ Reprint (Orig + 2 copies)   ☐ Technical Report (Orig + 2 copies)

☐ Manuscript (1 copy)   ☒ Final Progress Report (Orig + 2 copies)

                                ☐ Related Materials, Abstracts, Theses (1 copy)

CONTRACT/GRANT NUMBER: DAAG5598101155

REPORT TITLE: Designing Polymer Blends Through Modeling and Simulation

is forwarded for your information.

SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

Final Progress Report

(1) Statement of the Problem Studied

Our aim was to determine the phase behavior and dynamics of polymer blends and composites. In particular, we used theoretical models and computer simulations to establish guidelines for promoting the uniform dispersion (exfoliation) of clay sheets in polymer melts. In addition, our goal was to determine how the coupling between phase separation and wetting interactions in polymeric composites effects the structural evolution and phase behavior of the material.

(2) Summary of Most Important Results

We combined a density functional theory (DFT) with a self-consistent field model (SCF) to calculate the phase behavior of thin, oblate colloidal particles that are coated with surfactants and dispersed in a polymer melt. These coated particles represent organically modified clay sheets. By integrating the two methods, we can investigate the effect of the surfactants' characteristics (grafting density and length) and the polymer-surfactant interaction energy on the polymer-clay phase diagram. Depending on the values of these critical parameters and the clay volume fraction, the system can be in an isotropic or nematic phase (which corresponds to an exfoliated composite). The system can also form a smectic, crystal, columnar, or "house-of-cards" plastic solid, as well as a two-phase (immiscible) mixture. Using this model, we isolated conditions that lead to the stabilization of the homogeneous, exfoliated phases (the isotropic and nematic regions) and to the narrowing of the immiscible two-phase regions.

We developed a computer simulation for the dynamic behavior of a phase-separating binary mixture that contains mobile, solid particles. The system models "filled polymers", which contain not only a blend of different macromolecules, but also solid fillers. We focused on the case where one of the components preferentially wets the surface of the particles. By combining a mesoscopic, coarse-grained description of the fluids with a discrete model for the particles, we show that the addition of hard particles significantly changes both the speed and the morphology of the phase separation. To probe the late-stage properties of the system, we also developed a mean-field rate-equation model for the mixture. The results indicate that the phase separation is arrested in the late stage; the "steady-state" domain size depends strongly on both the particle diffusion constant and the particle concentration. To obtain insight into the effects of processing on the properties of such composites, we also investigated the behavior of the binary fluid/particle mixture under shear. For sufficiently large particle densities, we find that the anisotropic growth caused by the imposed shear is destroyed by the randomly moving particles, and the domains are isotropic in shape even for large shear strains. Finally, we applied our models to mixtures of diblock copolymers and fillers. Overall, our findings reveal how the solid additives can be used to tailor the morphology of the complex mixture, and thereby control the macroscopic properties (such as mechanical integrity) of the composite.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends not only on the characteristics of the copolymers, but also on the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we develop a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, the theory predicts new ordered phases,

where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

(3) Papers Published in Peer-Reviewed Journals

Thompson R, Ginzburg VV, Matsen M, Balazs, AC Predicting the Mesophases of Copolymer/Nanoparticle Composites SCIENCE 292 (5526): 2469-2472 JUNE 29 2001

Ginzburg VV, Balazs AC Calculating phase diagrams for nanocomposites: The effect of adding end-functionalized chains to polymer/clay mixtures ADV MATER 12 (23): 1805-1809 DEC 1 2000

Huh J, Ginzburg VV, Balazs AC Thermodynamic behavior of particle/diblock copolymer mixtures: Simulation and theory MACROMOLECULES 33 (21): 8085-8096 OCT 17 2000

Kuznetsov DV, Balazs AC Phase behavior of end-functionalized polymers confined between two surfaces J CHEM PHYS 113 (6): 2479-2483 AUG 8 2000

Ginzburg VV, Gibbons C, Qiu F, et al. Modeling the dynamic behavior of diblock copolymer/particle composites MACROMOLECULES 33 (16): 6140-6147 AUG 8 2000

Huh J, Balazs AC Behavior of confined telechelic chains under shear J CHEM PHYS 113 (5): 2025-2031 AUG 1 2000

Balazs AC Interactions of nanoscopic particles with phase-separating polymeric mixtures CURR OPIN COLLOID IN 4 (6): 443-448 DEC 1999

Peng GW, Qiu F, Ginzburg VV, et al. Forming supramolecular networks from nanoscale rods in binary, phase-separating mixtures SCIENCE 288 (5472): 1802-1804 JUN 9 2000

Singh C, Balazs AC Effect of polymer architecture on the miscibility of polymer/clay mixtures POLYM INT 49 (5): 469-471 MAY 2000

Balazs AC, Ginzburg VV, Qiu F, et al. Multi-scale model for binary mixtures containing nanoscopic particles J PHYS CHEM B 104 (15): 3411-3422 APR 20 2000

Kuznetsov DV, Balazs AC Scaling theory for end-functionalized polymers confined between two surfaces: Predictions for fabricating polymer/clay nanocomposites J CHEM PHYS 112 (9): 4365-4375 MAR 1 2000

Ginzburg VV, Singh C, Balazs AC Theoretical phase diagrams of polymer/clay composites: The role of grafted organic modifiers MACROMOLECULES 33 (3): 1089-1099 FEB 8 2000

Ginzburg VV, Peng G, Qiu F, et al. Kinetic model of phase separation in binary mixtures with hard mobile impurities PHYS REV E 60 (4): 4352-4359 Part B OCT 1999

Balazs AC, Singh C, Zhulina E, et al. Modeling the phase behavior of polymer/clay nanocomposites ACCOUNTS CHEM RES 32 (8): 651-657 AUG 1999

Ginzburg VV, Balazs AC Calculating phase diagrams of polymer-platelet mixtures using density functional theory: Implications for polymer/clay composites MACROMOLECULES 32 (17): 5681-5688 AUG 24 1999

Qiu F, Ginzburg VV, Paniconi M, et al. Phase separation under shear of binary mixtures containing hard particles LANGMUIR 15 (15): 4952-4956 JUL 2 99

Zhulina E, Singh C, Balazs AC Attraction between surfaces in a polymer melt containing telechelic chains: Guidelines for controlling the surface separation in intercalated polymer-clay composites LANGMUIR 15 (11): 3935-3943 MAY 25 1999

Ginzburg VV, Qiu F, Paniconi M, et al. Simulation of hard particles in a phase-separating binary mixture PHYS REV LETT 82 (20): 4026-4029 MAY 17 1999

Sun T, Balazs AC, Jasnow D Dynamics of the phase behavior of a polymer blend under shear flow PHYS REV E 59 (1): 603-611 Part B JAN 1999

Balazs AC, Singh C, Zhulina E Modeling the interactions between polymers and clay surfaces through self-consistent field theory MACROMOLECULES 31 (23): 8370-8381 NOV 17 1998

Lyatskaya Y, Balazs AC Modeling the phase behavior of polymer-clay composites MACROMOLECULES 31 (19): 6676-6680 SEP 22 1998

(4) Participating Personal

Most recently, the project provided postdoctoral training for V.Ginzburg, J. Huh and D. Kuznetsov. Corey Gibbons was an undergraduate who worked on the project and was a co-author on the following paper: Ginzburg VV, Gibbons C, Qiu F, et al. Modeling the dynamic behavior of diblock copolymer/particle composites MACROMOLECULES 33 (16): 6140-6147 AUG 8 2000